

PARAMAGNETIC RESONANCE OF Cr^{3+} IN MAGNESIUM TUNGSTATE

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The EPR spectrum of trivalent chromium ion in synthetic crystals of magnesium titanate is investigated. The magnetic axes and the constants of the spin Hamiltonian, including the hfs constant for the odd isotope of chromium, are determined. The spin-lattice relaxation time at 4.2°K is determined in two wavelength regions.

MAGNESIUM tungstate, MgWO_4 , crystallizes in the monoclinic system, space group $P2/c$.^[1] A method for growing monocrystals of this substance has been described by Van Uitert and Soden;^[2] the crystals we prepared by this method for our investigations measured up to $2 \times 3 \times 5$ mm.

An EPR spectrum consisting of two groups of lines was observed at room temperature in crystals grown without the special introduction of impurities. We established that one of these groups belongs to the trivalent iron ion Fe^{3+} , the spectrum of which has been described by Peter.^[3] Regarding the other group, which consists of significantly weaker lines, we assumed that it belonged to the EPR spectrum of the Cr^{3+} ion substitutionally replacing the Mg^{2+} ion in the crystalline lattice. This assumption was supported by the fact that the lines of this group were intensified when chromic oxide was added to the melt and also by the presence of a hyperfine structure characteristic of the odd isotope of chromium. The principal measurements were made on crystals containing 0.1% as many chromium ions as magnesium ions.

The EPR spectrum of Cr^{3+} in MgWO_4 is described by a spin Hamiltonian of the form

$$\hat{\mathcal{H}} = g_z \beta H_z \hat{S}_z + g_x \beta H_x \hat{S}_x + g_y \beta H_y \hat{S}_y + D(\hat{S}_z^2 - 5/4) + E(\hat{S}_x^2 - \hat{S}_y^2), \quad (1)$$

where \hat{S}_x , \hat{S}_y , and \hat{S}_z are the spin component operators; H_x , H_y , and H_z are the projections of the steady magnetic field on the corresponding magnetic axes; β is the Bohr magneton. For the isotope Cr^{53} there will be additional terms in Eq. (1) for the hyperfine structure.

In the 3 cm wavelength region one observes two EPR absorption lines, corresponding to the following transitions between levels with magnetic quantum numbers M : $-1/2 \rightarrow 1/2$ and $-3/2 \rightarrow 3/2$ (weak

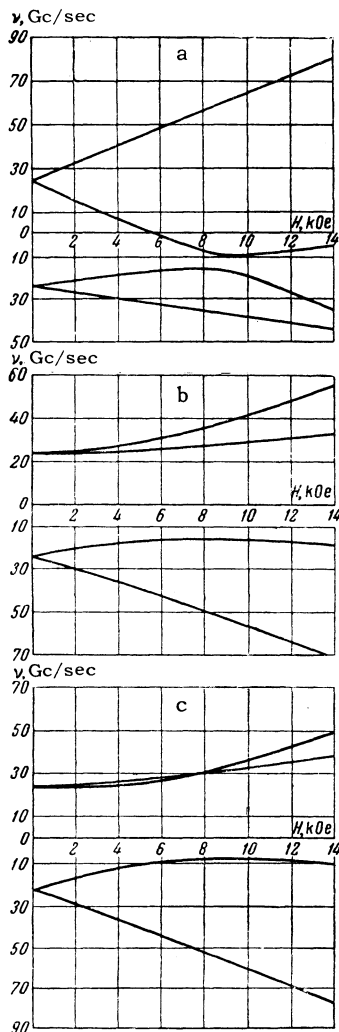
field classification of levels). The angular dependence of the spectrum was investigated, permitting the determination of the directions of the magnetic axes x , y , z relative to the crystal axes a , b , c . The latter were found on the basis of an analysis of a free stereographic projection constructed from three Laue photographs and an x-ray vibration photograph. Use was also made of Peter's data^[3] on the relation between the crystal and magnetic axes of Fe^{3+} . We found that the z , x , and y axes of Cr^{3+} coincide respectively with the a , b , and c crystal axes within an accuracy of one degree (as is known,^[1] the angle between the a and c axes is $89^\circ 40'$). It is to be noted that all Cr^{3+} ions are magnetically equivalent.

In order to determine the spin Hamiltonian constants with high accuracy, it is necessary to observe at least one absorption line corresponding to a transition between the Kramers doublets. This condition was successfully fulfilled in a shorter wavelength region, where the position of the line corresponding to the transition $-1/2 \rightarrow 3/2$ was measured at certain orientations of the external magnetic field. The data yielded the following values for the constants:

$$\begin{aligned} g_z &= 1.966 \pm 0.002, \\ g_x &= g_y = 1.960 \pm 0.002, \\ 2D &= +47.7 \pm 0.1 \text{ Gc/sec}, \\ E &= +1.84 \pm 0.05 \text{ Gc/sec}. \end{aligned}$$

The sign of D was determined from a comparison of the intensities of the transitions $-1/2 \rightarrow 1/2$ and $-3/2 \rightarrow 3/2$ at 290 and 4.2°K. The figure gives the results of a calculation of the energy levels for certain orientations of the external magnetic field based on these values for the constants.

The width of the $-1/2 \rightarrow 1/2$ line as observed in the 3 cm region was about 20 Oe for a Cr^{3+} ion



Energy levels for Cr^{3+} in MgWO_4 in an external magnetic field: (a) H along the z axis; (b) H along the x axis; (c) H along the y axis.

concentration of 0.1% (relative to Mg) and 14 Oe for a concentration of 0.007%. However, when the

external magnetic field is situated in the ac plane and is rotated from the a axis by 4° toward the side of the acute angle between a and c , the line width decreases sharply to 14 and 7 Oe, respectively. Apparently, the broadening of the line as the magnetic field is inclined away from the indicated direction has an inhomogeneous character.

At the place where the line width is a minimum, the hfs belonging to the isotope Cr^{53} can be resolved. We found the absolute value of the hfs constant A to be $0.0018 \pm 0.0001 \text{ cm}^{-1}$.

Measurements of the spin lattice relaxation time T_1 of Cr^{3+} in MgWO_4 at 4.2°K were also undertaken. For the case when the external magnetic field is directed along the z axis, the magnitudes of T_1 for the transitions $-\frac{1}{2} \rightarrow \frac{1}{2}$ and $-\frac{3}{2} \rightarrow \frac{3}{2}$ are respectively 2.4 and 0.8 msec as determined by the continuous saturation method at 3 cm. The pulse method applied in the decimeter region gave 2.0 and 0.5 msec, respectively.

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